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(54) Title: INJECTION MOULDING

(57) Abstract: The invention provides the use in injection moulding or extrusion coating, preferably in injection moulding of liquids containers, closures and caps, of a HDPE comprising at least two polyethylene components having different molecular weight distributions wherein at least one of said components is an ethylene copolymer.

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Injection Moulding

The invention relates to improvements in and relating to high density polyethylenes (HDPE) and in particular to the use of HDPE for injection moulding.

HDPE is a polymer which is often used for the production by injection moulding of products used for packaging or containers. The HDPE materials conventionally used for these purposes are generally monomodal polyethylenes prepared using Ziegler-Natta catalysts.

Where products are produced by injection moulding, it is important that the warpage in the product be low as otherwise the physical appearance of the product is poor.

Moreover, where an injection moulded HDPE product is to be used to contain liquids where spillage would be environmentally undesirable, it is important that the moulded polymer is resistant to stress cracking. This may be measured by the environmental stress crack resistance (ESCR) test, a standardized ASTM test (e.g. ASTM D1693. Cond B).

The standard commercially available HDPE injection moulding materials however have unsatisfactorily low ESCR values and thus are unsuitable for the production of injection moulded containers or other packaging materials for liquid chemical products, such as liquid chemicals, glues, paints, varnishes, solvent-based soaps etc.

The polymers used for injection moulding are monomodal (ie. with a single peak in their molecular weight distributions). This is in order to avoid warpage.

However, despite the conventional wisdom that it is essential to use monomodal HDPE for injection moulding, we have now surprisingly found that by using bimodal or

multimodal HDPE wherein at least one of the polyethylene components is an ethylene copolymer, it is possible to produce injection moulded products with improved ESCR and warpage.

Viewed from one aspect the invention thus provides the use in injection moulding, preferably in injection moulding of liquids containers, caps and closures, of a HDPE comprising at least two polyethylene components having different molecular weight distributions wherein at least one of said components is an ethylene copolymer.

While the different components may both be ethylene copolymers and while one may be an ethylene homopolymer, the components cannot both be ethylene homopolymers. Where one of the components is an ethylene homopolymer, this is preferably the component with the lower weight average molecular weight (Mw), e.g. where Mw is 5000 to 100000 D, more preferably 20000 to 40000 D.

Viewed from a further aspect the invention provides an injection moulded liquids container, preferably a container for liquids comprising an organic solvent, the walls whereof are formed from a HDPE comprising at least two polyethylene components having different molecular weight distributions wherein at least one of said components is an ethylene copolymer.

Viewed from a further aspect the invention provides an injection or extrusion moulded cap or closure, preferably a cap or closure for a container for beverages or liquids comprising an organic solvent, which cap or closure is formed from a HDPE comprising at least two polyethylene components having different molecular weight distributions wherein at least one of said components is an ethylene copolymer.

Viewed from a further aspect the invention provides an HDPE for use in injection moulding, comprising at least two polyethylene components, wherein at least one said component is an ethylene copolymer and wherein at

least the component with the lowest weight average molecular weight is an ethylene homopolymer'.

By polyethylene is meant a polymer the majority by weight of which derives from ethylene monomer units. Minor comonomer contributions, e.g. up to 20% by weight more preferably up to 10% by weight, may derive from other copolymerizable monomers, generally C_{3-20} , especially C_{3-10} , comonomers, particularly singly or multiply ethylenically unsaturated comonomers, in particular C_{3-10} α -olefins such as propene, but-1-ene, hex-1-ene, 4-methyl-pent-1-ene etc. It may be noted that the term ethylene copolymer is used herein to relate to a polyethylene deriving from ethylene and one or more such copolymerisable comonomers. Moreover, the polyethylene may contain minor, e.g up to 10% by weight, preferably up to 5% by weight of other polymers, e.g. other polyolefins in particular polypropylenes, as well as additives such as colours, fillers, radiation stabilizers, antioxidants, etc., generally in amounts of up to 10% by weight, preferably up to 5% by weight.

By HDPE is meant a polyethylene having a density of 940 to 980 kg/m³, preferably 945 to 975 kg/m³, especially 950 to 965 kg/m³ and a crystallinity of 60 to 90%, preferably 70 to 90%.

The HDPE according to the invention is a bimodal or multimodal polymer. By bimodal (or multimodal), it is meant that the polymer consists of at least two fractions (components), one of which has a relatively low molecular weight and a relatively high density and another of which has a relatively high molecular weight and a relatively low density. Typically the molecular weight distribution (MWD) of a polymer produced in a single polymerization stage using a single monomer mixture, a single polymerization catalyst and a single set of process conditions (ie. temperature, pressure etc.) will show a single maximum, the breadth of which will depend on catalyst choice, reactor choice, process

conditions, etc, ie. such a polymer will be monomodal.

A bimodal or multimodal polyethylene may be produced by blending two or more monomodal polyethylenes having differently centred maxima in their MWDs. Alternatively and preferably the bimodal polyethylene may be produced by polymerization using conditions which create a bimodal or multimodal polymer product, e.g. using a catalyst system or mixture with two or more different catalytic sites, using two or more stage polymerisation process with different process conditions in the different stages (e.g. different temperatures, pressures, polymerisation media, hydrogen partial pressures, etc).

Such a bimodal (or multimodal) HDPE may be produced relatively simply by a multistage ethylene polymerization, e.g. using a series of reactors, with comonomer addition in only the reactor(s) used for production of the higher/highest molecular weight component(s). Examples of bimodal PE production are given in EP-A-778289 and WO92/12182.

If an ethylene homopolymer component is produced by slurry polymerization involving use of recycled diluent, that diluent may contain small amounts of higher α -olefins as contaminants. Likewise where an earlier polymerization stage has produced an ethylene copolymer component, small amounts of comonomer may be carried over to an ethylene homopolymerization stage. Accordingly, by ethylene homopolymer is meant herein a polymer containing at least 99.9% by weight of ethylene units. Likewise as in a multistage/multireactor polymerization using more than one catalyst system, the homopolymerization catalysts may be at least partially active during the copolymerization reaction, any copolymer component making up less than 5% by weight of the total polymer shall not be considered to be the lowest molecular weight component in an HDPE according to the invention.

The copolymer component(s) of the HDPE used according to the invention will generally contain at least 0.1% by weight, preferably at least 0.5% by weight of non-ethylene monomer units, e.g. 0.5 to 6% of such comonomer units.

The polymerization reactions used to produce the HDPE of the invention may involve conventional ethylene homopolymerization or copolymerization reactions, e.g. gas-phase, slurry phase, liquid phase polymerizations, using conventional reactors, e.g. loop reactors, gas phase reactors, batch reactors etc. (see for example WO97/44371 and WO96/18662). The catalyst systems used may likewise be any conventional systems, e.g. chromium catalysts, Ziegler-Natta and metallocene or metallocene:aluminoxane catalysts, either homogeneous or more preferably heterogeneous catalysts, e.g. catalysts supported on inorganic or organic particulates, in particular on magnesium halides or inorganic oxides such as silica, alumina or silica-alumina. For the preparation of the high molecular weight component in particular it is especially desirable to use supported Ziegler-Natta catalysts as the molecular weight can then conveniently be controlled using hydrogen. It is also possible to use supported metallocene catalysts as it is particularly straightforward to select desired molecular weights by appropriate selection of particular metallocenes. The metallocenes used will typically be group IVa to VIa metals (in particular Zr or Hf) complexed by optionally substituted cyclopentadienyl groups, e.g. groups carrying pendant or fused substituents optionally linked together by bridging groups. Suitable metallocenes and aluminoxane cocatalysts are widely described in the literature, e.g. the patent publications of Borealis, Hoechst, Exxon, etc.

Typically and preferably however the HDPE will be prepared using multistage polymerization using a single

catalyst system or a plurality of catalyst systems, e.g. two or more metallocenes, one or more metallocenes and one or more Ziegler-Natta catalysts, two or more chromium catalysts, one or more chromium catalysts and one or more Ziegler-Natta catalysts, etc. Especially preferably the same catalyst system is used in the different polymerization stages, e.g. a catalyst system as described in EP-A-688794.

The properties of the HDPE used according to the invention preferably have the following values:

Low molecular weight component:

MFR₂ of 50-1000 g/10 min, preferably 200-800 g/10 min, measured according to ISO 1133 at 190°C and under 2.16 kg load;

weight average molecular weight of 5-50 kD, preferably 20-40 kD;

preferably a homopolymer or a copolymer with density higher than 965 kg/m³, most preferably a homopolymer;

comprises 10-90% by weight, preferably 40-60% by weight of the total polyethylene in the composition.

High molecular weight component:

Has molecular weight and comonomer content such that the final polymer composition has the desired preset MFR and density;

weight average molecular weight of 150-400 kD;

comprises 10-90% by weight, preferably 40-60% by weight of the total polyethylene in the composition, i.e. low mw:high mw component weight ratio is 10:90 to 90:10, preferably 40:60 to 60:40.

Final polymer composition:

MFR₂ of 2-100 g/10 min, preferably 3-50 g/10 min, in particular 4-20 g/10 min, measured according to ISO 1133 at 190°C and under 2.16 kg load;

weight average molecular weight of 80-200, preferably 100-180 kD;

molecular weight distribution (ratio of the weight average molecular weight to the number average molecular weight) of 5-100, preferably 10-60, more preferably 14-45;

density of 940-980 kg/m³, preferably 945-975 kg/m³, in particular 950-965 kg/m³;

comonomer content of 0.2-10% by weight, preferably 1-3% by weight, as measured by FTIR;

crystalline melting point between 120 and 140°C, as determined by DSC analysis;

crystallinity of 60-90%, as determined by DSC analysis.

Injection moulded article made from the polymer composition:

ESCR F₅₀ higher than 10 h, preferably higher than 40 h, measured according to ASTM D1693, Condition B;

improvement in ESCR, measured as above, relative to a standard unimodal material HE7004 (manufactured and sold by Borealis) of 50-1000%, preferably of 500-1000%;

E-modulus of at least 800 MPa (measured according to ISO 527-2);

Impact strength of 30-200 kJ/m² (measured according to ISO 8256-A).

Such HDPE may typically be prepared in a one or more stage polymerization, with the catalyst systems and process conditions in the individual stages being selected to produce polyethylene components of average molecular weights 5 to 100 kD and 150 to 400 kD in abundances of 1:9 to 9:1.

For injection moulding of the resultant HDPE, conventional moulding equipment may be used, e.g. operating at an injection temperature of 190 to 275°C, Typically containers produced in this fashion will have

a volume of 100 mL to 100 L and caps and closures will typically have maximum dimensions of 10 to 600 mm.

The injection moulding compositions of the invention have the further advantage of improved flow. This may be demonstrated using the 'spiral test'. In this procedure an Engel ES330/65 injection moulding apparatus is used with a spiral mould with a depth of 1, 2 or typically 3 mm. The composition flow rate at 230°C under 300, 500 and 700 bar follow up pressures is determined on the length of flow in the spiral. Typically a composition according to the invention with an MFR₂ value of about 4 g/10 min behaves like a conventional polyethylene with MFR₂ of about 8 g/10 min. See Table 1 below.

Table 1

| Modality | MFR ₂ * (g/10 min) | Flow (cm) at pressure (p) (bar) | | |
|----------|----------------------------------|---------------------------------|-------|-------|
| | | p=300 | p=500 | p=700 |
| Bimodal | 4 | 32.6 | 47.5 | 61.3 |
| Unimodal | 2 | 21.5 | 32.3 | 41.6 |
| Unimodal | 4 | 27.1 | 39.8 | 52.5 |
| Unimodal | 8 | 35.2 | 50.2 | 65.2 |
| Unimodal | 12 | 40.8 | 57.2 | 72.5 |

* measured according to ISO 1133

Besides being useful for injection moulding, it has also been found that the bimodal and multimodal HDPEs used according to the invention are particularly useful for extrusion coating, e.g. of paper or other substrates, producing coatings with low water vapor permeability and good coating draw down rates. Such use of the bimodal and multimodal HDPE's (especially ones with densities in excess of 935 kg/m³) forms a further aspect of the invention.

Viewed from a still further aspect the invention provides an HDPE comprising at least two polyethylene

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components, wherein at least one said component is an ethylene copolymer and wherein at least the component with the lowest weight average molecular weight is an ethylene homopolymer and having the following characteristics:

MFR₂ of from 2 to 100;
mean weight average molecular weight of from 80 to 200 kD;
MWD of from 5 to 100;
weight average molecular weight of a low molecular weight fraction of 20 to 40 kD;
weight average molecular weight of a high molecular weight fraction of 150 to 400 kD;
weight ratio of said low molecular weight fraction to said high molecular weight fraction of 10:90 to 90:10;
melting point 120 to 140°C;
density 940 to 950 kg/m³;
comonomer content 0.2 to 10% by weight; and
crystallinity 60 to 90%.

Viewed from a yet further aspect the invention provides an HDPE moulding composition comprising a particulate HDPE having the following characteristics:

MFR₂ of from 2 to 100;
mean weight average molecular weight of from 80 to 200 kD;
MWD of from 5 to 100;
weight average molecular weight of a low molecular weight fraction of 20 to 40 kD;
weight average molecular weight of a high molecular weight fraction of 150 to 400 kD;
weight ratio of said low molecular weight fraction to said high molecular weight fraction of 10:90 to 90:10;
melting point 120 to 140°C;
density 940 to 950 kg/m³;
comonomer content 0.2 to 10% by weight; and
crystallinity 60 to 90% together with at least one additive or further polymer.

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Viewed from another aspect the invention provides an injection moulded article formed at least in part from an HDPE having the following characteristics:

MFR₂ of from 2 to 100;
mean weight average molecular weight of from 80 to 200 kD;
MWD of from 5 to 100;
weight average molecular weight of a low molecular weight fraction of 20 to 40 kD;
weight average molecular weight of a high molecular weight fraction of 150 to 400 kD;
weight ratio of said low molecular weight fraction to said high molecular weight fraction of 10:90 to 90:10;
melting point 120 to 140°C;
density 940 to 950 kg/m³;
comonomer content 0.2 to 10% by weight; and
crystallinity 60 to 90%.

The invention will now be described further by reference to the following non-limiting Examples:

Example 1

Blended Bimodal HDPE

Two bimodal polyethylene compositions (Samples 1 and 2) were prepared by mixing two of the three polyethylene components (A, B and C) listed in Table 1 into blends using an extruder (Werner & Pfleider ZSK 30W) operating at 193-194°C.

Table 1

| Component Property | Component | A | B | C |
|------------------------------|-----------|-----|-----|------|
| Mw (kD) | | 190 | 400 | 28 |
| Mn (kD) | | 6 | 56 | 2.5 |
| MWD | | 32 | 7 | 11 |
| MFR ₂₁ (g/10 min) | | 33 | 0.1 | 400* |
| Density (kg/m ³) | | 955 | 927 | 974 |
| *MFR ₂ | | | | |

Sample 1 comprised 40% wt component C and 60% wt component A. Sample 2 comprised 60% wt component C and 40 wt% component B.

The properties of the blends are shown in Table 2 below.

Example 2Reactor Produced Bimodal HDPE

Into a 50 dm³ loop reactor, operated at 80°C and 65 bar, was introduced 1 kg/hour ethylene, 22 kg/hour propane, 2g/hour hydrogen and the polymerization catalyst of Example 3 of EP-B-688794 (loaded on 20 micron silica) in a quantity such that PE production rate was 6.8 kg PE/hour. The MFR₂ and density of the product are estimated at 30 g/10 min and 970 kg/m³ respectively.

The slurry was continuously removed from the loop reactor and introduced into a second loop reactor having a volume of 500 dm³ operating at 95°C and 60 bar. Additional ethylene, propane and hydrogen were added so as to produce a polyethylene at 27 kg/hour having MFR₂ 500 g/10 min and density 974 kg/m³. The polymer (still containing the active catalyst) was separated from the

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reaction medium and transferred to a gas phase reactor where additional hydrogen, ethylene and 1-butene comonomer were added so as to produce a polyethylene at 70 kg/hour having MFR₂ 4 g/10 min and density 953 kg/m³. The fraction of high MFR (low MW) material in the total polymer was thus 40%. Three samples, denoted 3, 4 and 5, were produced in this manner.

The properties of samples 1 to 5 are set out in Table 2 below.

A commercially available unimodal reference material HE 7004 (Borealis) was similarly evaluated. The results are designated R1.

Table 2

| Samples: | 1 | 2 | 3 | 4 | 5 | R1 | R2 |
|---|-------|-------|-------|-------|-------|------|-----|
| Mw Weight Average | 121 | 170 | 102 | 106 | 105 | 105 | 70 |
| Molecular Weight (kD) | | | | | | | |
| Mn Number Average | 4.2 | 4.1 | 7 | 7.4 | 7.2 | 16 | 13 |
| Molecular Weight (kD) | | | | | | | |
| MWD | 29 | 41 | 14.5 | 14.3 | 14.2 | 6 | 5.5 |
| MFR ₂ g/10 min ¹ | 2.6 | 1.7 | 3.9 | 3.2 | 4.8 | 4.0 | 12 |
| Density (kg/m ³) ² | 963 | 956 | 953 | 953 | 957 | 954 | 964 |
| Ratio LMW/HMW | 40/60 | 60/40 | 40/60 | 40/60 | 40/60 | | |
| ESCR, F50 (hours) ³ | 46 | 86 | 46 | 43 | | 9 | |
| ESCR improvement (%) | 411 | 856 | 411 | 378 | | 0 | |
| E-modulus (kPa) ⁴ | 1080 | 930 | 880 | 830 | | 850 | |
| Comonomer content (wt %) | 0.5 | 1.1 | 1.4 | 1.4 | | <0.1 | |

¹MFR₂ determined at 190°C using 2.16 kg load according to ISO 1133

²Density determined using ISO 1183

³ESCR, F50 determined using ASTM D1693, Cond.B

⁴E-modulus determined using ISO 527-2

Table 2 clearly shows the bimodal HDPE to have superior ESCR properties.

Samples 3 and 4 in particular had excellent warpage and shrinkage properties.

Example 3

Injection Moulding

Using Samples 1 and 2 of Example 1, pails were produced by injection moulding. Specimens were cut from the walls of the pails and placed in a liquid containing 25 or 40% turpentine. Both samples produced products which showed approvable swell behaviour and stiffness in this test.

Example 4

Extrusion Coating

Extrusion coating runs were made on a beloit pilot line using UG paper of 70 g/m² weight. The coating was a coextruded structure comprising a commercially available LDPE (LE 7518 from Borealis) and Sample 5 of Example 2 above at coating weights of 20 and 10 g/m² respectively. The structure was thus paper -LE 7518 - sample 5. Corona treatment was used to improve adhesion to paper. Different line speeds were tested between 100 and 500 m/min and line behaviour was acceptable even at the highest speed. A sample was taken and tested for water vapour transmission rate (WVTR) (measured at 90% relative humidity and 38°C according to ASTM - E96). WVTR was found to be 10.3 g/m²/24 hours.)

By way of comparison, a coated structure was produced in the same way using a commercially available unimodal HDPE (HE 7012 from Borealis, R2 in Table 2 above) in place of Sample 5. The WVTR was found to be $11.8\text{g/m}^2/24$ hour, i.e. a higher value even though the density of R2 is greater than that of Sample 5.

The bimodal HDPE thus has improved barrier properties relative to conventional materials.

Claims:

1. The use in injection moulding or extrusion coating of a HDPE comprising at least two polyethylene components having different molecular weight distributions wherein at least one of said components is an ethylene copolymer.
2. Use as claimed in claim 1 of a said HDPE for injection moulding of liquids containers, closures or caps.
3. Use as claimed in either of claims 1 or 2 of an HDPE having the following characteristics:
MFR₂ of from 2 to 100;
mean weight average molecular weight of from 80 to 200 kD;
MWD of from 5 to 100;
weight average molecular weight of a low molecular weight fraction of 20 to 40 kD;
weight average molecular weight of a high molecular weight fraction of 150 to 400 kD;
weight ratio of said low molecular weight fraction to said high molecular weight fraction of 10:90 to 90:10;
melting point 120 to 140°C;
density 940 to 950 kg/m³;
comonomer content 0.2 to 10% by weight; and
crystallinity 60 to 90%.
4. An injection moulded liquids container the walls whereof are formed from a HDPE comprising at least two polyethylene components having different molecular weight distributions wherein at least one of said components is an ethylene copolymer.
5. A container as claimed in claim 4 formed from a said HDPE having the following characteristics:

MFR₂ of from 2 to 100;
mean weight average molecular weight of from 80 to 200 kD;
MWD of from 5 to 100;
weight average molecular weight of a low molecular weight fraction of 20 to 40 kD;
weight average molecular weight of a high molecular weight fraction of 150 to 400 kD;
weight ratio of said low molecular weight fraction to said high molecular weight fraction of 10:90 to 90:10;
melting point 120 to 140°C;
density 940 to 950 kg/m³;
comonomer content 0.2 to 10% by weight; and
crystallinity 60 to 90%.

6. An injection or extrusion moulded cap or closure, which cap or closure is formed from a HDPE comprising at least two polyethylene components having different molecular weight distributions wherein at least one of said components is an ethylene copolymer.

7. A cap or closure as claimed in claim 6 formed from a said HDPE having the following characteristics:

MFR₂ of from 2 to 100;
mean weight average molecular weight of from 80 to 200 kD;
MWD of from 5 to 100;
weight average molecular weight of a low molecular weight fraction of 20 to 40 kD;
weight average molecular weight of a high molecular weight fraction of 150 to 400 kD;
weight ratio of said low molecular weight fraction to said high molecular weight fraction of 10:90 to 90:10;
melting point 120 to 140°C;
density 940 to 950 kg/m³;
comonomer content 0.2 to 10% by weight; and
crystallinity 60 to 90%.

8. An extrusion coated structure having at least one extruded layer formed from a HDPE comprising at least two polyethylene components having different molecular weight distributions wherein at least one of said components is an ethylene copolymer.

9. A structure as claimed in claim 8 wherein said at least one extruded layer is formed from a HDPE having the following characteristics:

MFR₂ of from 2 to 100;

mean weight average molecular weight of from 80 to 200 kD;

MWD of from 5 to 100;

weight average molecular weight of a low molecular weight fraction of 20 to 40 kD;

weight average molecular weight of a high molecular weight fraction of 150 to 400 kD;

weight ratio of said low molecular weight fraction to said high molecular weight fraction of 10:90 to 90:10;

melting point 120 to 140°C;

density 940 to 950 kg/m³;

comonomer content 0.2 to 10% by weight; and

crystallinity 60 to 90%.

10. A structure as claimed in claim 8 or claim 9 wherein said HDPE has a density of 955-975 kg/m³.

11. An HDPE for use in injection moulding or extrusion coating, comprising at least two polyethylene components, wherein at least one said component is an ethylene copolymer and wherein at least the component with the lowest weight average molecular weight is an ethylene homopolymer.

12. An HDPE comprising at least two polyethylene components, wherein at least one said component is an ethylene copolymer and wherein at least the component

with the lowest weight average molecular weight is an ethylene homopolymer, and having the following characteristics:

MFR₂ of from 2 to 100;
mean weight average molecular weight of from 80 to 200 kD;
MWD of from 5 to 100;
weight average molecular weight of a low molecular weight fraction of 20 to 40 kD;
weight average molecular weight of a high molecular weight fraction of 150 to 400 kD;
weight ratio of said low molecular weight fraction to said high molecular weight fraction of 10:90 to 90:10;
melting point 120 to 140°C;
density 940 to 950 kg/m³;
comonomer content 0.2 to 10% by weight; and
crystallinity 60 to 90%.

13. An HDPE moulding composition comprising a particulate HDPE as defined in claim 12 together with at least one additive or further polymer.

14. An injection moulded article formed at least in part from an HDPE having the following characteristics:

MFR₂ of from 2 to 100;
mean weight average molecular weight of from 80 to 200 kD;
MWD of from 5 to 100;
weight average molecular weight of a low molecular weight fraction of 20 to 40 kD;
weight average molecular weight of a high molecular weight fraction of 150 to 400 kD;
weight ratio of said low molecular weight fraction to said high molecular weight fraction of 10:90 to 90:10;
melting point 120 to 140°C;
density 940 to 950 kg/m³;
comonomer content 0.2 to 10% by weight; and

crystallinity 60 to 90%.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L23/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | US 4 451 873 A (TYLER DAVID O ET AL) 29 May 1984 (1984-05-29) abstract; claims 1-14 column 4, line 39-44; tables 1,2 column 5, line 25 -column 6, line 70 column 2, line 40,41 | 1-14 |
| X | SEPPALA J V ET AL: "Effect of polymerization temperature on the polymerization of ethylene with dicyclopentadienylzirconiumdichloride/meth ylalumoxane catalyst" EUROPEAN POLYMER JOURNAL,GB,PERGAMON PRESS LTD. OXFORD, vol. 32, no. 3, 1 March 1996 (1996-03-01), pages 331-335, XP004075819 ISSN: 0014-3057 abstract | 1-14 |

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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